

SPECIFICATION AMENDMENTS

On page 1, insert above line 1, insert--Priority Claim

The present application claims priority on European Patent Application 03076114.2 filed 15 April 2003.--

Paragraph on line 1 of page 1 has been amended as follows:

-- The invention is directed related to a process to prepare a mixture comprising carbon monoxide and hydrogen from a carbonaceous feed by performing a partial oxidation reaction and an endothermic steam reforming reaction.--

Paragraph on line 3 of page 2 has been amended as follows:

--Suitably, there is a desire to operate a convective steam reformer and make use of the hot gasses of a partial oxidation. A problem when combining these processes is that the temperature of the gasses as obtained in a partial oxidation reaction are high, e.g. between 1100 and 1500 °C. If such gasses are to be used to provide the heat in a convective steam reformer there are practical problems have to be overcome, such as one have to avoid that breakage of the materials used in the CSR convective steam reformer reactor do not break as a result of mechanical failure. There is thus a desire to obtain a combined POX and CSR process, which overcomes these practical problems.--

Paragraph on line 16 of page 2, ending on line 6 of page 3, has been amended as follows:

-- This object is achieved with the following process. Process The invention provides a process for the preparation of hydrogen and carbon monoxide containing gas from a carbonaceous feedstock by performing the following steps:

- (a) partial oxidation partially oxidizing of a carbonaceous feedstock in ~~an~~ a vertically oriented tubular partial oxidation reactor vessel comprising a burner at its upper end thereby obtaining a first gaseous product of hydrogen and carbon monoxide,
- (b) catalytic catalytically steam reforming a carbonaceous feedstock in a Convective Steam Reformer Zone thereby obtaining a steam reformer product,
- (c) reducing the temperature of the first gaseous product of step (a) by mixing this product with the steam reformer product of step (b),

- (d) contacting the mixture obtained in step (c) with a post reforming catalyst, and
- (e) providing the required heat for the convective steam reforming reaction zone in step (b) by convective heat exchange between the mixture obtained in step (d) and the steam reformer reactor zone thereby obtaining a hydrogen and carbon monoxide containing gas having a reduced temperature.--

On page 3, delete line 7-16.

On page 3, above line 17, insert--Brief Description of the Drawings--

On page 3, above line 20, insert the following paragraph:

-- By reducing the effluent of the partial oxidation by mixing with the effluent of the steam reformer and subsequently performing a post reforming step one can run the convective steam reformer at a lower temperature. The higher methane content of the steam reformer product as a result of operating the convective steam reformer at lower temperatures is balanced by performing the catalytic post reforming step in which part of the methane is converted to synthesis gas.--

Paragraph on line 20 of page 3 has been amended as follows:

-- The carbonaceous feedstock in step (a) is preferably a gaseous hydrocarbon, suitably methane, natural gas, associated gas or a mixture of C₁₋₄ hydrocarbons. Examples of gaseous hydrocarbons are natural gas, refinery gas, associated gas or (coal bed) methane and the like. The gaseous hydrocarbons suitably comprises mainly, i.e. more than 90 v/v%, especially more than 94%, C₁₋₄ hydrocarbons, especially comprises at least 60 v/v percent methane, preferably at least 75 percent, more preferably 90 percent. Preferably natural gas or associated gas is used. Preferably any sulphur sulfur in the feedstock is removed.--

Paragraph on line 32 of page 3, ending on line 3 of page 4 has been amended as follows:

-- Preferably the carbonaceous feed in both steps (a) and (b) is a gaseous feed as described above. In such a preferred embodiment, from 10 wt% to 90 wt%, more preferably from 20 wt% to 50 wt%, of the total gaseous feed to steps (a) and (b) is fed to step (b). --

Paragraph on line 22 of page 4 has been amended as follows:

--Contacting the feed with the oxygen containing gas in step (a) is preferably performed in a burner placed in a reactor vessel. To adjust the H₂/CO hydrogen to carbon monoxide ratio in the gaseous product obtained in the partial oxidation reaction in step (a), carbon dioxide and/or steam may be introduced into the feed. Preferably up to 15% volume based on the amount of gaseous product, preferably up to 8% volume, more preferably up to 4% volume, of either carbon dioxide or steam is added to the feed. As a suitable steam source, water produced in an optional downstream hydrocarbon synthesis, e.g. Fischer-Tropsch synthesis, may be used.--

Paragraph on line 1 of page 5 has been amended as follows:

-- The gaseous product of the partial oxidation reaction in step (a) typically has a temperature of between 1100 °C and 1500 °C and an H₂/CO hydrogen to carbon monoxide molar ratio of from 1.5 up to 2.6, preferably from 1.6 up to 2.2. --

Paragraph on line 5 of page 5 has been amended as follows:

-- Step (b) may be performed by well-known steam reforming processes, wherein steam and the gaseous hydrocarbon feed are contacted with a suitable reforming catalyst in a CSR convective steam reformer reactor. Preferably the CSR convective steam reformer reactor zone is present in a separate reactor vessel next to the POX partial oxidation reactor vessel. The convective steam reactor zone preferably comprises of a tubular reactor vessel provided with one or more tubes containing a reforming catalyst. Various designs for such a reactor are known and suited for the present invention. The design should be such that the steam reformer product and the synthesis gas used to provide heat are obtained as separate streams in such a reactor. An Example example of such a reactor concept is described in US-A-6224789 US Pat. No. 6224789. The steam reformer product may have a methane content of between 1 mol% and 30 mol% carbon relative to the carbon as hydrocarbon in the feed to step (b). In a preferred embodiment the methane content is between 1 mol% and 10 mol% carbon and preferably between 2 mol% and 5 mol% carbon relative to the carbon as hydrocarbon in the feed to step (b).--

Paragraph on line 25 of page 5, ending on line 20 of page 6 has been amended as follows:

--The catalyst and process conditions as applied in the steam reformer reactor tubes may be those known by the skilled person in the field of steam reforming. Suitable catalysts comprise nickel optionally applied on a carrier, for example alumina. The space velocity of the gaseous feed is preferably from 700 liter to 1000 litre liter (S.T.P.)/litre liter catalyst/hour, wherein S.T.P. means Standard Temperature of 15 °C and pressure of 1 bar abs. The steam to carbon (as hydrocarbon and CO carbon monoxide) molar ratio is preferably below 1 and more preferably from 0.5 up to 0.9. If such low steam to carbon ratio's ratios are applied in step (b) the catalyst preferably comprises a Group VIII metal. More preferably, the catalyst comprises (a) an oxidic support material and (b) a coating comprising between about 0.1 wt% and about 7.0 wt% of at least one of the metals selected from of the group consisting of Pt, Ni, Pd and Co, preferably platinum; said support material comprising:

(i) at least 80 wt% of ZrO₂ which has been calcined at a temperature up to about 670 °C before the application of said coating; (ii) 0.5-10 mol% of at least one oxide selected from the group consisting of oxides of Y, La, Al, Ca, Ce and Si, preferably La₂O₃. Examples of such catalysts are, for example, the catalyst described in EP-A-695279. Preferably, the feed also comprises an amount of CO2 carbon dioxide, wherein preferably the CO2 carbon dioxide over carbon (as hydrocarbon and CO carbon monoxide) molar ratio is from 0.5 up to 2. The product gas of step (b) preferably has a temperature of from 600 °C up to 1000 °C and a H₂/CO hydrogen to carbon monoxide molar ratio of from 0.5 up to 2.5. --

Paragraph on line 21 of page 6, ending on line 6 of page 7 has been amended as follows:

--In Step (c) the temperature of the first gaseous product of step (a) is reduced by mixing this product with the steam reformer product of step (b). This mixing may be performed in the partial oxidation reactor vessel, in a separate mixing vessel or within a separate CSR convective steam reformer reactor vessel. If the mixing is performed in the POX partial oxidation reactor vessel it is preferably performed by feeding the steam reformer product to the lower end, preferably in the lower half of the POX partial oxidation reactor vessel, spaced away from the burner. In this manner, no significant methane conversion takes place during mixing and a reduction of temperature will result. Due to mixing, at a position spaced away from the burner, of the product of the partial oxidation

reaction having a temperature of between 1100 °C and 1500 °C and steam reformer product having a ~~considerable~~ considerably lower temperature, a temperature reduction relative to the temperature of the product of the partial oxidation reaction of between 250 °C and 500 °C may be achieved.--

Paragraph on line 7 of page 7 has been amended as follows:

-- In step (d) the mixture obtained in step (c) is contacted with a post reforming catalyst. This may suitably be achieved by passing the gaseous mixture through a bed of suitable reforming catalyst. This catalyst bed may be position in the ~~POX~~ partial oxidation reactor vessel, in a separate vessel or in the ~~CSR~~ convective steam reformer reactor vessel, also depending on the location at which step (c) is performed. When step (c) is performed in the ~~POX~~ partial oxidation reactor vessel, step (d) is preferably performed in a catalyst bed positioned just below the inlet of the steam reforming product in said vessel. --

Paragraph on line 18 of page 7 has been amended as follows:

-- The methane is preferably converted in a step (d) in which also a temperature reduction is achieved of suitably between 20 °C and 70 °C and preferably between 40 °C and 60 °C. The mixture obtained in step (d) having a reduced methane content preferably has a temperature of between 950 °C and 1100 °C and more preferably a temperature between 980 °C and 1050 °C. The methane conversion in step (d) is suitably between 10 wt% and 50 wt%.--

Paragraph on line 29 of page 7, ending on line 2 of page 8 has been amended as follows:

-- The effluent of step (d) is subsequently fed to the ~~CSR~~ convective steam reformer reactor zone wherein the gasses supply heat to said zone and a cooled final synthesis gas product is obtained. In step (e) the temperature of the metal wall surfaces of the materials of the internals in the ~~CSR~~ convective steam reformer reactor are preferably maintained below 1100 °C.--

Paragraph on line 3 of page 8 has been amended as follows:

-- The above process may be performed in a process configuration as illustrated in Figure 1. Figure 1 illustrates a ~~CSR~~ convective steam reformer reactor (44) and a ~~POX~~ partial oxidation reactor vessel (51). The ~~CSR~~ convective steam reformer reactor (44) is

provided with one or more parallel positioned reactor tubes (21) filled with a bed (22) of steam reforming catalyst, comprising a passageway (23) for hot gas, namely the effluent of step (d). One reactor tube (21) may suitably be provided with between 1-10 passageways (23). A third tube sheet (32) is present at the lower end of the reactor vessel (44) defining a space (33) which fluidly connects the vessel inlet (38) for the mixture as obtained in step (d) with the inlet of the passageways (23) which penetrate the tube sheet (32) via openings (34) which are preferably larger than the passageway (23) itself. The fact that the passageways are not fixed in the tube sheet (32) is advantageous because it allows the combined reactor tubes (21) and passageways (23) to freely thermally expand in the reactor vessel (44) at start-up and cool down situations. The lower ends of the passageway which extends into the lower space (33) may preferably be made from heat resistant materials, like for example ceramics, because of the high temperatures present in said space due to the fact that here the mixture as obtained in step (d) enters the CSR convective steam reformer reactor via vessel inlet (38).--

Paragraph on line 29 of page 8, ending on line 18 of page 9 has been amended as follows:

-- The outlet opening (35) of the reactor tubes (21) comprising the catalyst bed (22) are positioned just above said tube sheet (32). The steam reforming product being discharged from said opening (35) will enter space (36) defined as the space between tube sheets (40) and (32). This space (36) fluidly connects the vessel outlet (39) for the steam reforming product with the openings (35). The space (36) may suitably be provided with flow directing baffles which will direct the flow of steam reforming product in a zig zag flow through said space thereby optimising optimizing the contact of the hot steam reformer product gas and the external surface of the reactor tubes (21) present in said space. In use, part of the steam reforming product being discharged from openings (35) will leave the reactor vessel via outlet (39) and part will leave space (36) via openings (34) to space (33) by operating the reactor such that the pressure in space (36) is higher than the pressure in space (33). In use, preferably from 0 wt% to 60 wt% and more preferably from 0 wt% to 40 wt% of the steam reformer product, as being discharged from openings (35), may enter space (33) to be mixed with the effluent of step (d).--

Paragraph on line 30 of page 9, ending on line 11 of page 10 has been amended as follows:

-- Figure 1 also shows a POX partial oxidation reactor vessel (51) provided with a burner (52) to which natural gas and oxygen (50) are provided ~~too~~. Steam reformer product as discharged at (39) is fed to the POX partial oxidation reactor vessel (51) via conduit (55) and openings (57) such to perform mixing step (c) at a distance below burner (52) substantially outside the circulating flow around the burner (52), which flow is present in the upper region of the reactor vessel. This results in that In this way, no significant conversion of the methane as present in the steam reformer product takes place. Figure 1 also shows a post reforming catalyst bed (53) and a connecting conduit (56) to provide the mixture as obtained in step (d) to step (e). In step (e) this mixture is provided to passageways (23) to supply heat to the steam reforming catalyst bed (22). --

Paragraph on line 12 of page 10 has been amended as follows:

--The synthesis gas as such obtained by the above process may advantageously be used as feedstock for a Fischer-Tropsch synthesis process, methanol synthesis process, a dimethyl ether synthesis process, an acetic acid synthesis process, ammonia synthesis process or to other processes which use a synthesis gas mixture as feed, such as for example, processes involving carbonylation and hydroformylation reactions. To steps (a) and (b) preferably recycle gases are fed. These recycle gasses are obtained in, for example, the above exemplified[[,]]processes which use the synthesis gas as prepared by the process according to the invention. These recycle gasses may comprise C₁₋₅ hydrocarbons, preferably C₁₋₄ hydrocarbons, more preferably C₁₋₃ hydrocarbons. These hydrocarbons, or mixtures thereof, are gaseous at temperatures of 5-30 °C (1 bar), especially at 20 °C (1 bar). Further, oxygenated compounds, e.g. for example, methanol, dimethylether, and acetic acid may be present.--

Paragraph on line 30 of page 10, ending on line 13 of page 11 has been amended as follows:

-- The invention is especially directed to the above process for the preparation of hydrogen and carbon monoxide containing gas (synthesis gas), wherein additional steps (f) and (g) are also performed. In step (f) the synthesis gas is catalytically converted using a Fischer-Tropsch catalyst into a hydrocarbons comprising stream. In step (g) the hydrocarbons comprising stream of step (f) is separated into a hydrocarbon product and a gaseous recycle stream. Suitably, the hydrocarbon product are these comprises hydrocarbons having 5 or more

carbon atoms, preferably having 4 or more carbon atoms and more preferably having 3 or more carbon atoms. The gaseous recycle stream may comprise normally gaseous hydrocarbons produced in the synthesis process, nitrogen, unconverted methane and other feedstock hydrocarbons, unconverted carbon monoxide, carbon dioxide, hydrogen and water.--

Paragraph on line 14 of page 11 has been amended as follows:

– In step (g) the recycle stream is fed to step (a) and/or (b). Preferably, the recycle stream is supplied to the burner of step (a) or directly supplied to the upper region of the partial oxidation reactor. –

Paragraph on line 22 of page 11 has been amended as follows:

– Step (f) and (g) may be performed by the well known Fischer-Tropsch processes which are for example the Sasol process and the Shell Middle Distillate Process. Examples of suitable catalysts are based on iron and cobalt. Typical reactor configurations include slurry reactors and tubular reactors. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-4943672 US Pat. No. 4943672, US-A-5059299 US Pat. No. 5059299, WO-A-9934917 and WO-A-9920720, all of which are herein incorporated by reference.–

On page 12 above line 1, insert --We claim:--